

1254487

THE UNITED STATES OF AMERICA

"TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

November 30, 2004

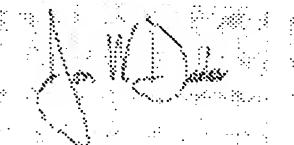
THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE.

APPLICATION NUMBER: 60/480,643

FILING DATE: June 23, 2003

RELATED PCT APPLICATION NUMBER: PCT/US04/20108

Certified by



Jon W Dudas

Acting Under Secretary of Commerce
for Intellectual Property
and Acting Director of the U.S.
Patent and Trademark Office



BEST AVAILABLE COPY

052527 U.S. PTO
06/23/03

PTO/SB/16 (10-01)

Approved for use through 10/31/2002. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

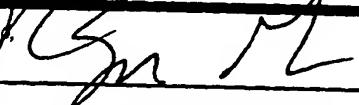
Express Mail Label No.

EL 823 269 441 US

17602 U.S. PTO
60/480643
06/23/03

INVENTOR(S)					
Given Name (first and middle if any) James M.	Family Name or Surname Tour	Residence (City and either State or Foreign Country) Bellaire, Texas			
<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max) ELASTOMERS REINFORCED WITH CARBON NANOTUBES					
Direct all correspondence to:					
<input type="checkbox"/> Customer Number	CORRESPONDENCE ADDRESS				
OR	Type Customer Number here				
<input checked="" type="checkbox"/> Firm or Individual Name	Ross Spencer Garsson				
Address	Winstead Sechrest & Minick P.C.				
Address	P.O. Box 50784				
City	Dallas	State	Texas	ZIP	75250-0784
Country	U.S.A.	Telephone	(512) 370-2870	Fax	(512) 370-2850
ENCLOSED APPLICATION PARTS (check all that apply)					
<input type="checkbox"/> Specification	Number of Pages	4	<input type="checkbox"/> CD(s), Number		
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input checked="" type="checkbox"/> Other (specify)	Check; Postcard	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	<input type="checkbox"/> FILING FEE AMOUNT (\$)				
<input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees	\$80.00				
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: <u>23-2426</u>					
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.					
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input type="checkbox"/> No.					
<input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: <u>NASA-JSC-NCC-977,</u> <u>OSR 99091801 NASA JSC NCC-01-0203 JCFDA#43,001, NSR-DMR-0073046, AFOSR F49-01-1-0364</u>					

Respectfully submitted,

SIGNATURE TYPED or PRINTED NAME Ross Spencer GarssonTELEPHONE (512) 370-2870Date 06/23/2003REGISTRATION NO.
(if appropriate)
Docket Number:38,15011321-P069V1**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

BEST AVAILABLE COPY

PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (02-01)

Approved for use through 10/31/2002. OMB 0651-0032
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number	11321-P069V1
---------------	--------------

INVENTOR(S)/APPLICANT(S)

Given Name (first and middle [if any])	Family or Surname	Residence (City and either State or Foreign Country)
Jared L.	Hudson	Houston, Texas
Ramanan	Krishnamoorti	Bellaire, Texas
Koray	Yurekli	Houston, Texas
Cynthia A.	Mitchell	Houston, Texas

Number 1 of 1

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

BEST AVAILABLE COPY

Elastomers Reinforced with Carbon Nanotubes

Description of the invention:

General purpose The invention is the development of elastomers reinforced with functionalized single walled carbon nanotubes (SWNTs). Development of high strength elastomers with high breaking strains and low densities are crucial in many applications. The material with 1 wt % of a functionalized SWNT exhibits a three fold increase in the tensile modulus and strains-at-break of 6.5, a number almost identical to the un-reinforced system.

For example, while additives can be applied within elastomers to make them have a higher tensile modulus (stiffness), they generally cause a concomitant large reduction in the strain-at-break. More specifically as an example, polyisoprene shows a strain-at-break of 10 (i.e. 1000%). By adding 20-30% by weight carbon black, the tensile modulus could increase 10-fold (10x), but the strain-at-break would fall to 1.25 (25%), hence it would no longer respond like an elastomer, but as a thermoplastic.

Therefore, to be able to stiffen elastomers while retaining the elongation-to-break properties is a significant advance. Elastomers are a very large industry including: tires, belts, hoses, seals, O-rings, etc. that affect industries such as automotive, engine, aerospace, oil drilling and refining, etc.

Although demonstrated here with SWNT, this should work well for multi-walled tubes as well since we have demonstrated the functionalization of those species.

Technical description Cross-linked elastomers were prepared using amine terminated poly(dimethylsiloxane) (PDMS) with weight average molecular weight of 5,000 daltons and a functionalized SWNT. Crosslink densities, estimated on the basis of swelling data in toluene, indicated that the polymer underwent crosslinking at the ends of the chains. This crosslinking was thermally initiated and found to occur only in the presence of the aryl alcohol functionalized SWNTs. The crosslink could have been via a hydrogen-bonding mechanism between the amine and the free hydroxyl group, or via attack of the amine on the ester linkage to form an amide. Tensile properties examined at room temperature indicated three fold increase in the tensile modulus of the elastomer, with rupture and failure of the elastomer occurring at a strain of 6.5. See appendix for details.

Elastomers find wide applications from sealants to tires to coatings. In many of these applications it is crucial for the elastomers to possess high strengths and yet be light and ductile.

Combines the unique properties of SWNTs with those of elastomer while maintaining low density and high strain-at-break. Other nanoparticles such as layered silicates can provide similar low density and high strain-at-break but do not possess the extraordinary mechanical, thermal and electrical properties of SWNTs.

The invention is a process involving the following steps:

1. Preparation of functionalized SWNT
2. Blending of polymer and functionalized SWNTs in common dispersing solvent (toluene)
3. Mix and homogenize for 24 hours
4. Precipitate in non - solvent (methanol) or rapidly evaporate and remove solvent.
5. Vacuum dry nanocomposite for 24 hours with vacuum of < 10 milli Torr at room temperature
6. Heat nanocomposite to 160 °C for 18 hours under vacuum.

Although the demonstration here is only for PDMS, the technique should work for a wide range of elastomers (see e.g., polyisoprene, polybutadiene, polyisobutylene, halogenated polyisoprene, halogenated polybutadiene, halogenated polyisobutylene, low-temperature epoxy, EPDM terpolymers, nitriles, and combinations thereof) and a wide range of functional nanotubes. It is not restricted to the system shown here. The key is having these long nanotube structures linked within the elastomer matrix. It will likely also work with multi-walled carbon nanotubes.

Grant or Contract Number:

To JMT: NASA-JSC-NCC-9-77, OSR 99091801, NASA TiMS NCC-01-0203 CFDA #43.001, the NSF (NSR-DMR-0073046) and the AFOSR (F49620-01-1-0364)

Detailed results and procedures.

Crosslinked samples of an amine-terminated polydimethylsiloxane ($M_w \sim 5000$, Aldrich) with aryl-substituted nanotubes (with alcohol terminus)* were performed at 170 °C in a heated press after initial degassing in a vacuum oven overnight at 120 °C. During the thermal cure, the samples were subjected to a forces of 1 ton and continuously subject to vacuum. Control samples of crosslinked PDMS were prepared using a vinyl terminated PDMS ($M_w \sim 5000$, HULS) and crosslinked with TEOS. Crosslink densities for the two samples were found within measurement errors to be similar based on swelling in toluene and hexane.

Tensile stress – strain measurements were performed on three micro-dumbbell specimens, prepared by molding in a high temperature press with vacuum suction applied to the specimen holders, at a test temperature of 25 °C and an Instron cross-head speed of 0.5"/min. The data shown in Figure 1 demonstrate the significantly higher modulus of the SWNT based PDMS elastomer as compared to the control sample with no SWNT. Moreover, the strains at break for the two samples are comparable. Based on a total of six samples for the nanocomposites and the unfilled elastomer:

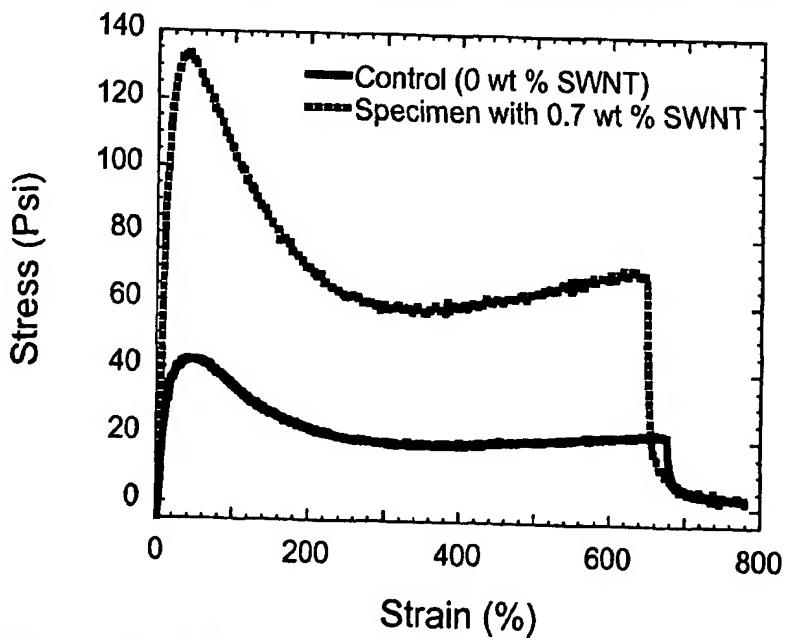
$$\frac{Y_{\text{nano}}}{Y_{\text{control}}} = 3.2 \pm 0.2$$

$$\epsilon_{\text{nano}}^{\text{break}} = 630 \pm 20 \%$$

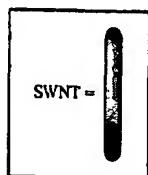
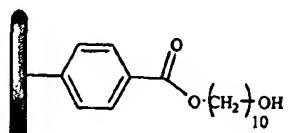
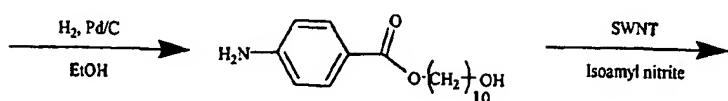
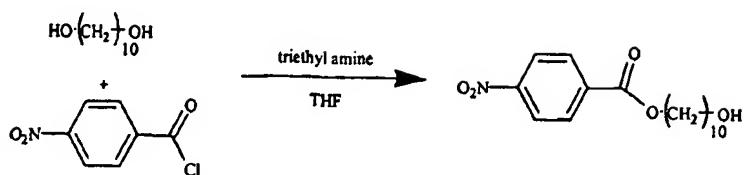
$$\epsilon_{\text{Control}}^{\text{break}} = 670 \pm 25 \%$$

where Y_{nano} and Y_{control} are the tensile modulus estimated based on the linear behavior at low strain values for the nanocomposite and the control sample respectively, and $\epsilon_{\text{nano}}^{\text{break}}$ and $\epsilon_{\text{Control}}^{\text{break}}$ are the values of the strain at break for the nanocomposite and the control sample respectively.

Figure 1. *The functionalized SWNT sample used was prepared in the following manner. The functionalization protocol is



described in Dyke, C. A.; Tour, J. M. "Solvent-Free Functionalization of Carbon Nanotubes," *J. Am. Chem. Soc.*, 2003, 125, 1156 -1157.



What is claimed is:

1. A method of reinforcing elastomers comprising the steps of:
 - a) preparing a plurality of functionalized carbon nanotubes;
 - b) blending the functionalized carbon nanotubes with an elastomeric polymer in a dispersing solvent to form a mixture;
 - c) removing the dispersing solvent from the mixture; and
 - d) heating the mixture to thermally initiate crosslinking.
2. The method of Claim 1, wherein the carbon nanotubes are single-wall carbon nanotubes.
3. The method of Claims 1 or 2, wherein the functionalized carbon nanotubes comprise aryl functional moieties.
4. The method of Claims 1-2 or 3, wherein the elastomeric polymer is an amine terminated poly(dimethylsiloxane).
5. The method of Claim 1-2 or 3, wherein the elastomeric polymer is selected from the group consisting of polyisoprene, polybutadiene, polyisobutylene, halogenated polyisoprene, halogenated polybutadiene, halogenated polyisobutylene, low-temperature epoxy, EPDM terpolymers, nitriles, and combinations thereof.
6. The method of Claims 1-4 or 5, wherein the dispersing solvent is toluene.

HOUSTON_1\656662\1
11321-G99999 06/20/2003

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/020108

International filing date: 23 June 2004 (23.06.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US

Number: 60/480,643

Filing date: 23 June 2003 (23.06.2003)

Date of receipt at the International Bureau: 06 December 2004 (06.12.2004)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



BEST AVAILABLE COPY
World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse